electronic states suggests that to some extent, correlation effects may be estimated from formaldehyde and ethylene. That is, the relative energy of the ground state should be shifted downward, while the $\pi \rightarrow \pi^*$ states should be shifted at least slightly upward.

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Thieno[3,4-*c*]thiophenes. Electronic Structure[1a]

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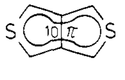
Abstract: Both the ground-state multiplicity, π stability ("aromaticity"), and ordering and energies of electronically excited and ionic states of the parent thieno[3,4-*c*]thiophene are studied theoretically in conjunction with a photoelectron spectral study of tetraphenyl[3,4-*c*]thienothiophene. It is shown that the thienothiophene system is "aromatic" like thiophene, but, nonetheless, unstable due to its particular HOMO structure and energy and the high reactivity resulting therefrom. Its characteristic properties, i.e., its particularly low first ionization energy (high HOMO orbital energy), low-energy first uv transition, strong charge transfer from sulfur to the carbon skeleton, and high 1,3-reactivity are rationalized on localized orbital interaction schemes.

The nature of bonding in the "nonclassical" condensed thiophenes remains a matter of some controversy.[2] With the aim of clarifying this situation we undertook a theoretical study of thieno[3,4-*c*]thiophene (**1**) and photoelectron (PE) spectral study of tetraphenylthieno[3,4-*c*]thiophene (**2**).



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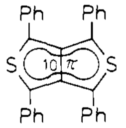

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Theoretical and Experimental Results

Using an unrestricted version of the extended[3] CNDO/S method[4] the ground state of **1** emerges as a triplet which is 1.4 kcal/mol more stable than the closed-shell singlet state.[5,6] The situation is, however, more than reversed when configuration interaction (taking account of all singly and doubly excited configurations up to a perturbative limit of 0.002 eV) is included. In this case, the lowest singlet is 31.8 kcal/mol more stable than the lowest triplet state. Accordingly, the ground state of **1** is anticipated to be a singlet state, in accord with what is found experimentally for **2**.[7]

A very important question concerns the "aromaticity" of thienothiophenes. We provide an answer on the basis of a method which recently[8] proved very satisfactory for that purpose. It consists here of calculating the total energy of **1** with and without sulfur π bonding and comparing the energy change with that obtained for thiophene. All calculations are done on an sp and spd basis by use of the CNDO/S procedure.[3] The conjugative stabilization energy is 94 (sp) and 138 (spd) kcal/mol for **1**, whereas 33 (sp) and 49 (spd) kcal/mol were predicted for thiophene.[8b] It is interesting to note that, accordingly, **1** is expected to be more "aromatic" than two thiophene molecules. A corresponding effect is detected in the magnitude of charge transfer from the two sulfur atoms to the carbon skeleton. It amounts to 0.72 (sp) and 0.66 e (spd) and is thus appreciably higher than for two thiophenes molecules (for one molecule: 0.22 (sp) and 0.16 e (spd)[8b]). From these data it appears that the d AO's in **1** play, just as in thiophene, no important role (as far as the ground state is concerned). The

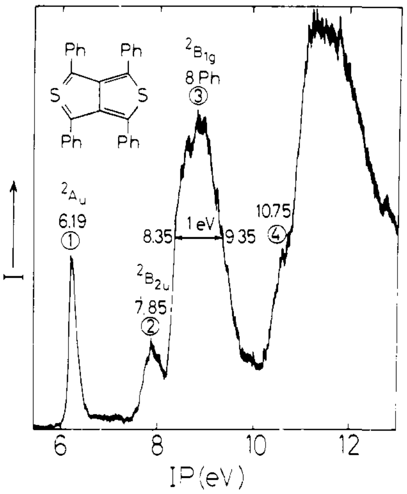


Figure 1. Photoelectron spectrum of tetraphenylthieno[3,4-*c*]thiophene with assignments. The numbers associated with each band refer to vertical ionization potentials in electron volts.

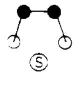
aforementioned extra effects (stabilization and charge transfer) will be rationalized in the next section.

An interesting point can be made from the uv PE spectrum of **2**, which is depicted in Figure 1. Bands 1 and 2 are π ionizations resulting from the thienothiophene central ring system, whereas the broad and intense ionization region 3 contains the third thienothiophene event and eight phenyl π events. The ordering of CNDO/S Koopmans[9] and improved[10] (by extensive configuration interaction including singly and doubly excited configurations as specified elsewhere[10b] and up to a perturbative limit of 0.002 eV) ion states comes out as ^2A_u, $^2B_{2u}$, and $^2B_{1g}$ for **1**. The low-lying ^2A_u state (6.19 eV for **2**) and thus *high-lying a_u orbital* as compared to their counterparts in naphthalene (8.15 eV[11]) is a focal point of interest to be rationalized in the next section.

2 is known[7] to possess a rather low-lying electronically excited molecular singlet state at 2.24 eV (maximum of the corresponding intense visible band in 1,2-dichloroethane solution). Our CNDO/S CI[3] calculations yield the state energies (with oscillator strengths of corresponding transitions greater than 0.001) for **1**: $^1B_{3u}$ ($a_ub_{3g}{}^*$) 2.79 (0.43), $^1B_{1u}$ ($b_{2u}b_{3g}{}^*$) 3.68 (0.11), B_{1u} ($a_ub_{1g}{}^*$) 5.24 (0.44). The low-lying $^1B_{3u}$ state is a consequence of the high-lying a_u HOMO as stated above. This factor in connection with the appropriate symmetry and topology of this orbital as depicted in the next section further helps to explain the strong tendency of dienophilic reagents to add to the 1,3-positions of **2**.[2,7]

Rationalization of Results

Figure 2 presents a calculated orbital interaction diagram for **1**.[8a,b] On the left are the basis orbitals of the carbon skeleton, on the right those of the two sulfur atoms, and in the middle their allowed combinations. The sulfur b_{2u}/carbon skeleton $b_{2u}{}^*$ orbital interaction corresponds to the well-known stabilizing and charge transferring interaction between the $b_1{}^*$ orbital of *cis*-butadiene and the sulfur p_z orbital (for a representation of these orbital see **3** below). Based on the data obtained (i.e., orbital energies of the interacting subunits in either the thiophene or thienothiophene cases and the π atomic orbital coefficients on the centers that are involved in the bonding process between the respective subunits), larger effects[12] than for thiophene are not anticipated. The extra charge transfer and extra stabilization found for **1** and mentioned in the preceding section originates from the sulfur b_{3g}/carbon skeleton b_{3g} interaction via a subsequent crossing of the resulting b_{3g} combination orbital with the carbon skeleton a_u* orbital. The filled b_{3g} combination is expected to be located at about −5 eV[13] (represented by the dashed level in Figure 2). Thus, by emptying it and filling the two electrons into the a_u* (leading to the a_u orbital of **1**) level the system gains roughly 4 eV[13] of orbital energy (2 eV for each electron involved, represented by a black arrow in Figure 2) and additional charge accumulates on the 1,3-positions.



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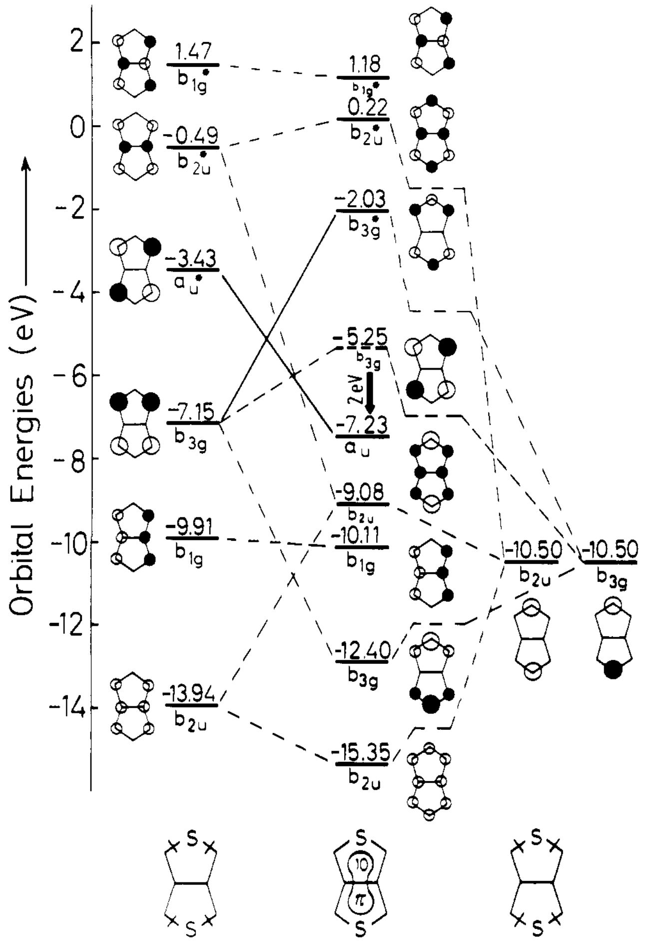
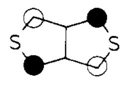


Figure 2. Calculated orbital interaction diagram of the carbon skeleton orbitals (on left) of thieno[3,4-*c*]thiophene and the sulfur π lone pair combinations (on right) for this system. The dashes across the C–S bonds symbolize interruption of π bonding. The fat solid lines draw attention to the crossing of the a_u* and b_{3g} orbitals leading to the a_u HOMO and b_{3g}* LUMO orbitals of the cyclic conjugated system. The dashed level of **1** indicates the hypothetical location[13] of the b_{3g} orbital and the black arrow the gain in orbital energy per electron due to the aforementioned orbital crossing.

The high energy of the a_u HOMO when referenced against its counterpart in naphthalene is a consequence of the missing stabilization from the π* orbitals of the ethylene units bridging the carbon skeleton in naphthalene. In **1**, the a_u orbital can only experience less effective d orbital stabilization (for a representation of the two HOMO's see **4** and **5** below, note especially the two bridging ethylenic π* subunit orbitals in **5**). As mentioned above it is this HOMO with correct symmetry and high



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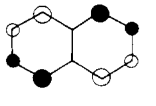

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coefficients in the 1,3 positions which makes the thienothiophenes good donor molecules for dienophilic reagents.

To summarize, the thienothiophenes are "aromatic" compounds like thiophene. Their high reactivity with respect to 1,3-additions follows from the HOMO energy and structure, as revealed by photoelectron spectroscopy. Thus, the hitherto unavailability of **1** appears to be a consequence of its high reactivity and not of its instability and **2** may be isolable because of a somewhat damped reactivity due to steric interference by the 1,3-phenyl substituents. Strictly speaking, these compounds are "nonclassical" only from the point of view of formal definition and representation.

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(12) These effects (orbital stabilization and charge transfer) are estimated on the basis of simple and well-known perturbational formulas.

(13) The reader is referred to Figure 2. Assuming a symmetrical splitting of the respective occupied subunit b_{3g} orbitals, the b_{3g} orbital of thienothiophene (filled) is expected to be located at (−7.15 + 1.90) eV = −5.25 eV. The found lowering of the b_{3g} sulfur lone pair combination is −1.9 eV.

Electron Transmission Studies of the Negative Ion States of Substituted Benzenes in the Gas Phase

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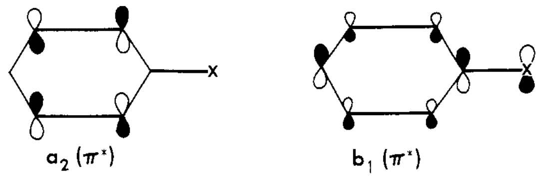
Abstract: Temporary negative ions of benzene, aniline, phenol, anisole, fluoro-, chloro-, and bromobenzene, formed in the gas phase by capture of electrons into the low-lying π^* orbitals, are studied by means of electron transmission spectroscopy. The electron affinities are determined and their relative values are interpreted in terms of resonance and inductive effects.

Negative ions of aniline, phenol, anisole, fluoro-, chloro-, and bromobenzene may be formed in the gas phase by capture of impacting electrons into the low-lying π^* orbitals. As in benzene and the alkyl-substituted benzenes, which we discussed in a previous communication,[1] these anions are short lived and decay by ejecting the electron into the continuum in times of typically 10^{-14} s or less. The formation of these transient anions is observable as sharp variations or "resonances" in the cross section for electron scattering from the neutral molecules. The impact energies at which the resonant structures are observed yield the magnitudes[2] of the gas-phase electron affinities (EA). In this communication we report the electron affinities of the above listed benzene derivatives determined by means of electron transmission spectroscopy (ETS).[3,4]

In Figure 1, we present the electron transmission spectra[5] of benzene, phenol, fluoro-, and chlorobenzene. The structure in the benzene spectrum, which is in good agreement with that found by others,[3b,3c,6] corresponds to the capture of an incident electron into the doubly degenerate $e_{2u}(\pi^*)$ orbital, yielding the X $^2E_{2u}$ ground electronic state of the benzene anion.[7] The lifetime of the anion is sufficiently long that a progression of vibrational levels of the symmetric breathing mode is observed.[8] With substitution on the ring, the degenerate $e_{2u}(\pi^*)$ orbital splits into $b_1(\pi^*)$ and $a_2(\pi^*)$ orbitals.[9] This splitting is particularly evident in the transmission spectrum of phenol. Similar results were found in aniline and anisole and the spectra are not shown. As shown below, the $a_2(\pi^*)$ orbital has nodes on the 1 and 4 carbons, while the $b_1(\pi^*)$ orbital does not possess nodes on any of the carbons.



The $-NH_2$, $-OH$, and $-OCH_3$ groups have small positive inductive effects[10] (which stabilize both A_2 and B_1 anion states) and large negative resonance effects[10] (which destabilize the B_1 state). We expect, therefore, that the ground state anions of aniline, phenol, and anisole will be slightly more stable than the ground state of $C_6H_6^-$ and will be of A_2 symmetry. On the other hand, the second anion states denoted by $\tilde{A}\,^2B_1$ should lie well above the $C_6H_6^-$ ground state. The